Synthesis, crystal structure and biological activity of a copper(II) complex with a 4-nitro-3-pyrazolecarboxylic ligand

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Abstract: The reaction of 4-nitro-3-pyrazolecarboxylic acid and Cu(OAc)2·H2O in ethanol resulted in a new coordination compound [Cu2(4-nitro-3-pzc)2(H2O)6]2H2O (4nitro-3pzc = 4-nitro-3-pyrazolecarboxylate). The compound was investigated by means of single-crystal X-ray diffraction and infrared spectroscopy. The biological activity of the complex was also tested. In the crystal structure of [Cu2(4nitro-3-pzc)2(H2O)6]2H2O, the Cu(II) ion is in a distorted [4+2] octahedral coordination due to the Jan–Teller effect. A survey of the Cambridge Structural Database showed that the octahedral coordination geometry is generally rare for pyrazole-bridged Cu(II) complexes. In the case of Cu(II) complexes with the 3-pyrazolecarboxylato ligands, no complexes with a similar octahedral coordination geometry have been reported. Biological research based on determination of the inhibition effect of the commercial fungicide Cabrio top and the newly synthesized complex on Ph. viticola were performed using the phytosanitary method.

Keywords: pyrazole; copper(II); coordination complexes; crystal structure; infrared spectra; inhibition effect.

INTRODUCTION

Pyrazole (pz) and pyrazole derivatives bearing different functional groups belong to an important class of ligands, capable of a variety of coordination modes with different metal ions.1,2 Apart from the confirmed biological signific-
ance of pz-based ligands and their metal complexes, these compounds are recognized as valuable components of novel materials (magnetic, energetic, luminescent and catalytic) and metal organic frameworks. The properties of these materials are frequently based on the ability of the pz ligands to produce bi- and poly-nuclear metal complexes coordinated by the two ortho positioned N donors. It is well known that the presence of substituents on the pz ring could significantly increase the ligand denticity and also influence the coordination geometry of metals. Among the pz-based bridging ligands, the 3,5-disubstituted pz derivatives are the most commonly investigated. Recently, the structural properties of Cu(II) and Co(II) complexes have been reported in which the dianion of 4-nitro-3-pyrazolecarboxylic acid (Scheme 1a) was used as a bridging ligand. These compounds are rare examples of metal complexes comprising a 3,4-disubstituted pz derivative as a bridge and also the first crystal structures of the transition metal complexes with ligands derived from 4-nitro-3-pyrazolecarboxylic acid (Scheme 1a).

Continuing interest in pyrazole-derived molecules, and particularly the bridging and structural behaviour of the 4-nitro-3-pyrazolecarboxylate ligand, a new binuclear complex [Cu2(4nitro-3pzcs)(H2O)6]2H2O, Scheme 1b, was synthesized. Here, the Cu(II) ion is found in a tetragonally distorted octahedral environment, dissimilar to previously reported five-coordinated Cu(II) complex with the same ligand. The novel complex was characterized by single-crystal X-ray diffraction and infrared spectroscopy. The antifungal activity of the compound was also tested for the fungi Ph. viticola using the phytosanitary method.

**EXPERIMENTAL**

**Synthesis**

The reaction of a warm ethanol (5 cm³) solution of Cu(OAc)2H2O (0.25 mmol, 0.0499 g) with 4-nitro-3-pyrazolecarboxylic acid (0.5 mmol, 0.08 g, dissolved in 6 cm³ ethanol) gave a green solution of the complex compound. The solution was allowed to crystallize. After two days, the green prism crystals of the complex of formula [Cu4(C4HN3O4)3(H2O)6]2H2O, measuring about 0.20 mm in size, were filtered and washed with a small amount of ethanol.
Yield: 0.0468 g (6.4%). Repeated synthesis under the same conditions and with the same ligand, where Cu(NO$_3$)$_2$3H$_2$O was used instead of Cu(OAc)$_2$H$_2$O, resulted in a complex of the same structural formula [Cu$_2$(C$_4$HN$_3$O$_4$)$_2$(H$_2$O)$_6$]2H$_2$O, also confirmed by X-ray structural analysis.

Methods

Infrared spectroscopy. Fourier-transform infrared (FTIR) attenuated total reflection (ATR) spectra of [Cu$_2$(4nitro-3pzc)$_2$(H$_2$O)$_6$]2H$_2$O were recorded using a Bruker Tensor 27 FTIR spectrometer, equipped with a mid-IR globar light source, a KBr beam splitter, a DLaTGS detector, and a Harrick MVP2 diamond ATR accessory at the Department of Mineralogy and Crystallography, University of Vienna. A total of 32 scans were accumulated between 4000 and 350 cm$^{-1}$ at a spectral resolution of 4 cm$^{-1}$. As the ATR spectra probe the complex index of refraction instead of pure absorption, a slight red shift of the band positions has to be considered.$^{13}$

X-Ray diffractometry and crystal structure solution. Single-crystal X-ray diffraction data for [Cu$_2$(4nitro-3pzc)$_2$(H$_2$O)$_6$]2H$_2$O were collected on a Nonius Kappa CCD single-crystal four-circle diffractometer (MoK$_{α_1}$-radiation, graphite monochromator), equipped with a 300 mm diameter capillary-optics colimator at the Department of Mineralogy and Crystallography, University of Vienna. The unit cell parameters were determined with HKL SCALEPACK (Nonius, 2005-2007). A complete sphere of reciprocal space ($φ$ and $ω$ scans) was measured. The intensity data were processed with the Nonius program suite DENZO-SMN$^{14}$ and corrected for absorption by the multi-scan method.$^{15}$ A monoclinic unit cell with a primitive Bravais lattice and space group symmetry $P2_1/n$ were derived from the reflection conditions and intensity statistics, both confirmed by consecutive structure refinement. The crystal structure was solved by direct methods incorporated in SHELXS and refined on $F^2$ by full-matrix least-squares using the SHELXL program.$^{16}$ Anisotropic displacement parameters were allowed to vary for all non-hydrogen atoms. The H atom of the pyrazole C atom was placed at the geometrically calculated position and refined using the riding model. H atoms belonging to coordinated and solvent water molecules were determined by the CALC–OH$^{17}$ program based on hydrogen-bonding interactions. These H atoms were then treated as riding with O–H distances fixed to 0.85 Å and the isotropic thermal parameters tied to the parent oxygen $U_{eq}(O)$. Relevant crystallographic details are listed in Table S-I of the Supplementary material to this paper.

Biological activity

The biological activity based on the determination of the inhibition effect of the commercial fungicide Cabrio top and the newly synthesized complex [Cu$_2$(4nitro-3pzc)$_2$(H$_2$O)$_6$]2H$_2$O on Ph. viticola were determined using the phytosanitary method. The diameters of fungal mycelium Ph. viticola as parameters of the inhibition effect were processed using variance analysis, while the testing was realized using the LSD test.$^{18}$

RESULTS AND DISCUSSION

Syntheses and characterization

The [Cu$_2$(4nitro-3pzc)$_2$(H$_2$O)$_6$]2H$_2$O complex was obtained in the reaction of ethanolic solutions of Cu(OAc)$_2$H$_2$O and 4-nitro-3-pyrazolecarboxylic acid. The same product was obtained when Cu(NO$_3$)$_2$3H$_2$O was used instead of Cu(OAc)$_2$H$_2$O. The FTIR ATR spectrum band positions and band assignments...
of [Cu$_2$(4nitro-3pzc)$_2$(H$_2$O)$_6$]$_2$H$_2$O (by comparison with literature) are summarised in Table S-II of the Supplementary material. A broad absorption band in the wavenumber region between ≈3600 and 2800 cm$^{-1}$ is assigned to the stretching vibrations of H$_2$O groups and is in agreement with the presence of medium strong to weak hydrogen bonds observed in the X-ray structure analysis. Using the distance–frequency correlation diagram for H bonds of Libowitzky,$^{19}$ an even wider range of donor–acceptor distances, i.e., ≈3.20 to 2.60 Å is expected. If, however, the wavenumber range above is constrained to the most intense region of the broad band, almost perfect agreement is obtained. Although the two superimposed narrow features at 3507 and 3157 cm$^{-1}$ may also well originate from O–H stretching vibrations of H$_2$O, an assignment to the N–H stretching vibration of pyrazole$^{20}$ for the former, and a C–H stretching vibration for the latter$^{21}$ is even more tempting.

The spectral region between 1700 and 1000 cm$^{-1}$ and the hump below 900 cm$^{-1}$ contains the bending/deformation mode of the H$_2$O molecules (1604 cm$^{-1}$ with asymmetric wing towards higher values) and a number of sharp bands that are characteristic of the vibrations of the pyrazole ring, the nitro group and the carboxylic unit. The latter shows the C=O stretching vibration as a shoulder at ≈1675 cm$^{-1}$ and the C–O stretching band at 1298 cm$^{-1}$. The C–O band position, however, is very tentative, as the direct coordination to Cu is assumed to influence the bond forces. The bending mode of the carboxylic group is assigned to the band at 806 cm$^{-1}$. The NO$_2$ nitro group reveals symmetric and antisymmetric stretching vibrations at 1354 and 1506 cm$^{-1}$, respectively, whereas the bending mode is observed at 858 cm$^{-1}$. For comparison, in pure 4-nitro-3-pyrazolecarboxylic acid these features are at 1370, 1510 and 860 cm$^{-1}$. The remaining bands (Table S-II) are assigned to the ring stretching modes (N–N, N–C and C–C) and the C–H bending modes of the pyrazole unit,$^{21,22}$ i.e., at 1535, 1461, 1401, 1391, 1207, 1137, 1110, 1007 and 750 cm$^{-1}$.

Description of crystal structure

The crystal structure of [Cu$_2$(4nitro-3pzc)$_2$(H$_2$O)$_6$]$_2$H$_2$O consists of binuclear complex units with copper(II) ions linked by a pair of dianionic pz ligands, Fig. 1a. The pz ligands simultaneously behave as N,O-chelating and N,N-bridging, giving rise to a five-membered chelate adjacent to the pz ring and to an approximately planar six-membered Cu$_2$N$_4$ metalocycle. Each copper centre is placed in a distorted octahedral environment, which exhibits pronounced elongation in the axial direction due to the Jahn–Teller effect (Fig. 1b). The coordination bonds to axial H$_2$O ligands are 2.5264(12) and 2.4123(11) Å for Cu–O6 and Cu–O7, respectively. The equatorial plane of this coordination polyhedron is formed by the NNO-donor set from the pz ligand and an additional H$_2$O ligand (Fig. 1). The lengths of equatorial coordination bonds (Table I) are comparable to
those found in the previously reported square-pyramidal \([\text{Cu}_2(4\text{nitro}-3\text{pzc})_2(\text{dmf})(\text{H}_2\text{O})]\) complex comprising the same pz ligand.\textsuperscript{10} Similar to previous findings, the pz ligand in \([\text{Cu}_2(4\text{nitro}-3\text{pzc})_2(\text{H}_2\text{O})_6]2\text{H}_2\text{O}\) displays asymmetrical coordination which is reflected in the corresponding Cu1–N1\textsuperscript{i}–N2 and Cu1–N2–N1 angles of 124.0(1) and 136.8(1)°, respectively (symmetry code: i = −x, −y, −z). The ring system is approximately flat. The dihedral angle between the central six-membered ring and the chelate ring is 3.2(1)°, while the inclination of the pz ring with respect to Cu2N4 and the chelate ring is 1.8(1) and 3.6(1)°, respectively. The Cu···Cu distance in this binuclear unit is 3.903(1) Å, which is slightly shorter than in a square-pyramidal Cu(II) complex, 3.945(1) Å.\textsuperscript{10}

![Crystal structure of \([\text{Cu}_2(4\text{nitro}-3\text{pzc})_2(\text{H}_2\text{O})_6]2\text{H}_2\text{O}\) complex](image)

**Fig. 1.** a) Crystal structure of \([\text{Cu}_2(4\text{nitro}-3\text{pzc})_2(\text{H}_2\text{O})_6]2\text{H}_2\text{O}\) and b) each Cu(II) ion is placed in the centre of tetragonally deformed octahedron.

**TABLE I.** Selected geometrical parameters; Symmetry code: (i) −x, −y, −z

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<th>Bond angle, °</th>
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<td></td>
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<td>172.52(4)</td>
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In the recently reported crystal structure of \([\text{Co}_2(4\text{nitro}-3\text{pzc})_2(\text{H}_2\text{O})_6]2\text{H}_2\text{O}\) complex with the same pz bridge,\textsuperscript{10} the Co(II) was found in an octahedral coordination environment equivalent to that of the Cu(II) ion in the title complex. The comparison of the geometrical features of the two octahedral complexes is given in the Supplementary material; here it is noted that their crystal arrangements are characterized by the same structural motifs, based on strong O–H···O hydrogen bonds (Table II). In both crystal structures, the presence of solvent water along with the coordinated water molecules significantly increases the complexity of the hydrogen bonding networks. Considering only the direct hydrogen bonding
between the complex units, each crystal structure is dominated by two interactions $O5$–$H5a$···$O2$ and $O6$–$H6a$···$O1$ (Table II). These interactions, formed between the coordinated water donors and carboxyl O acceptors, connect the complex units into corresponding zigzag chains (Fig. 2). An additional chain of directly bonded complex units is formed by the $O7$–$H7b$···$O6$ hydrogen bond that involves only the axially coordinated water ligands (Fig. 2). Similar to the Co(II) complex, this is the only case where the coordinated water acts as a hydrogen bonding acceptor, while all coordinated water molecules form significant hydrogen bonds as H-atom donors (all H atoms engaged). Contrary, the solvent water molecule simultaneously serves as donor and acceptor in four hydrogen bonds (Table II). These interactions connect the chains of directly bonded complex units into the three-dimensional crystal structure of $[\text{Cu}_2(4\text{nitro-3pzc})_2(\text{H}_2\text{O})_6]_2\text{H}_2\text{O}$ (Table II).

**TABLE II Hydrogen bond geometry; Symmetry code: (ii) $-x+1/2$, $+y-1/2$, $-z+1/2$; (iii) $x+1/2$, $-y+1/2$, $+z-1/2$; (iv) $x$, $+y+1$, $+z$; (v) $-x-1/2$, $+y-1/2$, $-z+1/2$; (vi) $x$, $y$, $z$.**

<table>
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<th>D–H···A</th>
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<th>D···A distance, Å</th>
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<td>2.755(2)</td>
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<td>3.006(2)</td>
<td>172</td>
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<tr>
<td>$O8$–$H8a$···$O2^{vi}$</td>
<td>2.08</td>
<td>2.861(2)</td>
<td>153</td>
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<td>$O8$–$H8a$···$O3^{vi}$</td>
<td>2.52</td>
<td>3.105(2)</td>
<td>127</td>
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</table>

Fig. 2. Crystal packing of $[\text{Cu}_2(4\text{nitro-3pzc})_2(\text{H}_2\text{O})_6]_2\text{H}_2\text{O}$. The three strongest hydrogen bonds formed between the complex units are presented by dashed lines.
Due to ability of pz ring to closely coordinate a pair of metal ions and support potential metal···metal interaction, pz-based ligands are widely used in the synthesis of polynuclear metal complexes. Among 1136 pz-bridged metal complexes deposited in the Cambridge Structural Database\textsuperscript{25} (CSD, version 5.40), those comprising at least one Cu centre represent the largest subgroup with 251 crystal structures. Interestingly, the Cu ion in these complexes is rarely found in an octahedral coordination environment. Thus, the CSD search for pz-bridged metal complexes comprising at least one Cu centre revealed 16 crystal structures with a six-coordinated Cu centre, 169 structures with a five-coordinated and 70 structures with a four-coordinated Cu centre.

The CSD does not contain binuclear Cu(II) complexes with 4-substituted-3-pyrazolecarboxylate ligands. In the case of Cu(II) complexes with the parent 3-pyrazolecarboxylato ligand, the CSD search revealed mononuclear (CSD refcode: DABRUW\textsuperscript{26}), binuclear (CSD refcodes: BEQGIQ\textsuperscript{27} BOYBOI\textsuperscript{28} and RUNXOO\textsuperscript{29}) and polynuclear complexes (CSD refcodes: BOYBUO\textsuperscript{28} LAGNIT\textsuperscript{30} QOFLAA\textsuperscript{31}); only in the mononuclear DABRUW\textsuperscript{26} was the Cu(II) found in an octahedral coordination environment. In all binuclear complexes, the Cu(II) is placed in a square pyramidal coordination environment, where fully deprotonated ligands bridge and chelate the pair of Cu(II) centres to form the square base of a polyhedron. Among these complexes, the binuclear BEQGIQ could be considered as a five-coordinated analogue of the title octahedral complex, with one axial H\textsubscript{2}O ligand less in the Cu(II) coordination sphere.\textsuperscript{27} In general, regardless of different coordination geometry, the binuclear, octahedral [Cu\(_2\)(4-nitro-3pc)\(_2\)(H\textsubscript{2}O)\(_6\)]\(_2\)H\textsubscript{2}O complex and the extracted square pyramidal 3-pyrazolecarboxylato Cu(II) complexes exhibit a number of common features. The comparison of the structural features of binuclear metal complexes with the 3-pyrazolecarboxylato ligands can be found in the Supplementary material to this paper.

**Biological activity**

A study on the biological efficacy of the applied compound under laboratory conditions was performed on nutrient medium potato dextrose agar (PDA), in Petri dishes of 90 mm in diameter. The solutions of the complex and a commercial fungicide (Table III) were poured into the nutrient medium at a temperature of 60 °C. The test was performed with five different concentrations of each compound and each was repeated four times. The initial concentration of all compounds was 0.12 %, and each subsequent composition was two times lower. Petri dishes with nutrient medium without added compounds served as controls. After the homogenization of the medium with the compound and agar solidification, mycelial fragments (6 mm in diameter) obtained from 10 days old pure cultures of *Ph. viticola* were placed in the centre of the Petri dishes. The inoculated Petri dishes were maintained in an incubator at 25 °C. Mycelia growth of the fungus
was measured when the colony in a control had covered about 2/3 of Petri dish diameter, which was the case after 10 days.

**TABLE III. Effect of commercial fungicide, \([\text{Cu}_2(4\text{nitro-3pzc})_2(\text{H}_2\text{O})_6]\)H_2O, Cu(OAc)_2H_2O and 4nitro-3pzc on the mycelia growth of the fungus Ph. viticola; Molar concentrations (c) of the studied compounds: 4nitro-3pzc: c_1 = 7.65\times10^{-3}, c_2 = 3.82\times10^{-3}, c_3 = 1.91\times10^{-3}, c_4 = 9.56\times10^{-4}, c_5 = 4.78\times10^{-4} \text{ M}; Cu(II) complex: c_1 = 2.05\times10^{-3}, c_2 = 1.03\times10^{-3}, c_3 = 5.13\times10^{-3}, c_4 = 2.56\times10^{-4}, c_5 = 1.28\times10^{-4} \text{ M}; Cu(OAc)_2\text{H}_2\text{O}: c_1 = 6.01\times10^{-3}, c_2 = 3.01\times10^{-3}, c_3 = 1.50\times10^{-3}, c_4 = 7.51\times10^{-4}, c_5 = 3.76\times10^{-4} \text{ M}**

![Image](Available on line at www.shd.org.rs/JSCS/)

The commercial fungicide expressed noticeably better inhibition effects than the applied complex. All concentrations of commercial fungicide showed statistically significant inhibition to colony growth of Ph. viticola, in comparison to the control. The studied complex did not express such a distinguished inhibition as a commercial fungicide, although there were concentrations among them that demonstrated a certain activity.

In contrast to the commercial fungicide that expressed a high inhibitory effect at all tested concentrations, the ligand showed a weak fungicidal effect.\(^{32}\) Namely, some tested pyrazole derivatives, depending on their structure and concentration, show a statistically significant inhibitory effect\(^{33}\) or a large fungicidal effect on pathogenic fungi that causes Phomopsis cane and leaf spot disease (patent application pending). Unlike the Cu(OAc)_2\text{H}_2\text{O} ligand, which at low concentrations (0.015 and 0.0075 %) shows a statistically significant inhibitory effect, but significantly lower than the commercial fungicide, while high concentrations of ligand (0.12 and 0.06 %) led to the increase in the diameter of the mycelium of the fungus. The weak inhibitory effect of the ligand and Cu(OAc)_2\text{H}_2\text{O} results in the present case also to the weak inhibitory effect of the complex compound on the examined fungus.

**CONCLUSIONS**

The dinuclear copper(II) complex comprising the dianion of 4-nitro-3-pyrazolecarboxylic acid as a bridge was synthesized by slow evaporation from ethanol at room temperature. The crystal structure of \([\text{Cu}_2(4\text{nitro-3pzc})_2(\text{H}_2\text{O})_6]\)H_2O contains Cu(II) ion in an octahedral coordination environment, significantly distorted due to the Jan–Teller effect. The three-dimensional arrangement of
Cu(II) COMPLEX WITH PYRAZOLE BRIDGE

[Cu₂(4nitro-3pzc)₂(H₂O)₆]₂H₂O is governed by strong intermolecular O–H⋯O hydrogen bonds involving the pyrazole ring substituents, coordinated water and the lattice water molecules. A CSD search revealed only rare cases of complexes in which pz-bridged Cu(II) ions display octahedral coordination geometry. In binuclear complexes of Cu(II) with the parent 3-pyrazolecarboxylato ligand, the metal ion is usually placed in a square pyramidal coordination environment. A commercial fungicide expressed noticeably better inhibition effects than the applied complex compound. All applied concentrations of the commercial fungicide showed statistically significant inhibition to colony growth of Ph. viticola, in comparison to the control.

SUPPLEMENTARY MATERIAL

Results of the CSD search, a Table giving crystal data, data collection and refinement details, and a Table concerning the FTIR results Additional data are available electronically at the pages of journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request. Supplementary tables of the crystal structures and refinements, notably the full list of bond lengths and angles, and the anisotropic displacement parameters have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 1940514. Copies of this information may be obtained free of charge from deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk.

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ИЗВОД

СИНТЕЗА, КРИСТАЛНА СТРУКТУРА И БИОЛОШКА АКТИВНОСТ КОМПЛЕКСА Cu(II) СА 4-НИТРО-3-ПИРАЗОЛКАРБОКСИЛНИМ ЛИГАНДОМ, [Cu₂(C₄H₃N₃O₄)₂(H₂O)₆]₂H₂O

МИЛИЦА КОСОВИЋ, славана новаковић, ЖЕЉКО ЛАТИМОВИЋ, НАДА МАРКОВИЋ, ТАМАРА БОРЕВИЋ, ЕУГЕН ЛИБОВИТЦКИ И ГЕРАЛЬД ГИЕСТЕР

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Реакцијом 4-нитро-3-пиразолине и Cu(OAc)₂H₂O у етанолу, синтетисан је нови комплекс [Cu₂(4nitro-3pzc)₂(H₂O)₆]₂H₂O, (4nitro-3pzc = дијанон 4-нитро-3-пиразолине). Комплекс је охарактерисан рендењском структурном анализом и инфрацрвном спектроскопијом. Такође су испитане биохемијске активности комплекса. У кристалној структури комплекса [Cu₂(4nitro-3pzc)₂(H₂O)₆]₂H₂O, Cu(II) јон се налази у октаедарском окружењу, значајно деформисаном услед јан–телеровог ефекта. Претрагом кристалографских база структурних података (CSD) установљено је да је октаедарска геометрија нетипична за мостне комплексе Cu(II) са лигандима пиразола. У случају комплекса Cu(II) са 3-карбокси пиразолом лигандима нису нађени комплекси са линион, октаедарском геометријом. Применом фитосанитарне методе испитана је инхибиторска активност комплекса на Ph. viticola у поређењу са комерцијалним фунгицидом Cabrio top.

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REFERENCES


